EXHIBIT "26"

This invention finds application where a thermoset impregnated web has utility. The saturated web will find use in shoe manufacture processes and other situations where a filler or backing material requiring rigidity with controlled flexibility is necessary during and after the manufacturing process.

The art has recognized that enhancement of physical properties of polymer-impregnated sheet material can be accomplished by additional treatment of the sheet with certain additives incorporated either in the impregnated composition or in the form of a post-impregnation treatment. U.S. Pat. No. 3,269,860 to Richardson et al describes a method for improving the delamination resistance and wet tensile strength of rubber latex saturated paper by incorporating an adduct of an isocyanate in the impregnating composition, drying the saturated paper web and heating the saturated paper web, usually at a temperature above about 285.degree. F., to release or activate the reactive group of the isocyanate adduct which persumably reacts with the rubber latex in the saturated paper and/or the paper itself.

SUMMARY

The composition of this invention can be used in a process where an intermediate stock material having thermoplastic characteristics is prepared. This stock material can then be stored until a manufacturing process molds the stock material at elevated temperatures when the crosslinking occurs to form a rigid product of controlled flexibility. This novel composition provides a means to avoid a second saturation dipping step to add the cross-linking agent. The novel composition consists essentially of from about 40 to about 70%, preferably 59%, by weight of a first monomer selected from styrene, vinylidene chloride, methyl methacrylate; butyl methacrylate and mixtures thereof, from about 60 to about 30% preferably 41% by weight of a second monomer selected from methylacrylate, ethylacrylate, butylacrylate, propylacrylate, 2-ethylhexylacrylate and mixtures thereof; and from about 0.5 to about 6.0%, preferably 2% based on monomers, by weight of N-methylolacrylamide. The latex composition has incorporated therein, in addition to the heat reactive cross-linking monomer N-methylolacrylamide, a sufficient amount of a neutralizing agent to adjust the pH value of the composition to 7.0 .+-. 1.0 so that a web saturated with the composition may be dried at temperatures up to 190.degree. F. without activating the cross-linking reaction. The dried web can thereafter be cross-linked at temperatures above 190.degree. F. to provide a thermoset product.

The novel process for preparing a saturated thermoset non-woven web having a cross-linking activation temperature above 190.degree. F. comprises the steps of preparing the composition described above, saturating a non-woven web with the composition, drying the composition saturated web at a temperature below the cross-linking activation temperature whereby a thermoplastic intermediate stock material having thermoset properties is produced.

DESCRIPTION

The porous, fibrous material which can be treated according to the invention includes porous woven and non-woven fiberous materials made conventionally from natural and synthetic fibers including cotton, ***asbestos,*** acetate, rayon, polyester, polyamide, polyvinyl alcohol, nylon, etc. as well as mixtures thereof. The composition of the invention has been found to be especially suited for treating porous, non-woven polyester web.

Porous, fibrous materials may be impregnated by dipping or immersing a sheet of the material into a bath containing the latex composition followed by squeeze rolling to remove the excess latex composition. The impregnated sheet is then dried for a limited period of time, i.e. 2 to 10 minutes, at a

controlled temperature, i.e. below about 190.degree. F. Sheets prepared in this manner are not cross-linked but are considered to be an intermediate product to be used in a later molding and forming operation where the cross-linking and curing occur.

In a commercial operation the web material is supplied on large reels. The web is continuously unwound and fed through a saturating pan where it is immersed in the saturating latex composition. The saturated web is then fed through one or more controlled temperature drying furnaces. In a preferred mode the saturated web emerges vertically from the saturating bath whereby any excess latex composition may be removed by gravity or squeeze rollers. Guide rollers feed the wet web into a vertical tower dryer. Additional guide rollers effectuate the web travel from a vertical to horizontal direction as the partially dry web follows zig-zag course in a generally horizontal direction through a tunnel dryer. The temperature of the dryers and the speed of the web are controlled so that the temperature of the exiting web is not above 180.degree. F. The saturated and dried web is spooled upon a take-up reel.

In a trial, webs of varying thickness were run through the process at approximately 15 to 18 feet per minute. The saturation pan was continuously fed with the latex composition. The saturated sheet went directly into a vertical tower dryer located 3-4 feet above the saturation pan, exiting in a horizontal plane into a tunnel dryer and finally to the wind-up stand. The dryer temperatures were varied from 150.degree. F. (56.degree. C.) to 230.degree. F. (110.degree. C.) in order to attain an exit web temperature of less than 190.degree. F. and preferably about 180.degree. F. The dryer temperature variations were due to the various base weight webs being processed.

The treated materials of the invention exhibit a porous fibrous structure containing fibers that are bonded or connected by the polymeric particles. The amount of latex composition in the porous fibrous material usually will range between about 9 to 16 oz. per square yard of non-woven structure, and preferably, about 12 to 15 oz. per square yard.

The latex component used in the composition of this invention is a copolymer of a first monomer selected form styrene, vinylidene chloride, methyl methacrylate, butylmethacrylate and mixtures thereof with a second monomer selected from methylacrylate, ethylacrylate, butylacrylate, propylacrylate, 2-ethylhexylacrylate and mixtures thereof. The cross-linking agent, N-methylolacrylamide, is specifically selected for its heat sensitive characteristics of not precross-linking when in combination with a neutralizing agent at pH values 7.0 .+-. 1.0.

Polymerization can be effected by simply combining monomers, emulsifier, initiators, etc. in a reaction vessel. Alternatively, and, preferably, the latex component of the invention is prepared by carrying out the aqueous polymerization reaction in the presence of a "seed" latex with continuous addition of monomer and emulsifier as is more fully described in U.S. Pat. No. 3,397,165 to Goodman et al. The emulsifiers and initiators useful within the scope of this invention are fully set forth in U.S. Pat. No. 3,397,165, the disclosure of which is incorporated by reference herein.

Briefly the method comprises introducing into the reaction vessel a relatively small amount of a polymer latex "seed" to provide nucleating sites for polymerization and adding, substantially continuously the first and second monomers along with the cross-linking agent and emulsifiers. The rate at which the monomers are added is such that the added monomers are associated with the polymer particles essentially as soon as the monomers enters the reaction zone, the formation of a separate monomer phase being prevented. The rate of emulsifier addition added continuously during polymerization to get good particles size distribution, is proportional to the rate of growth of particles

CDD12528

surface area. Preferably the monomers are added continuously to the aqueous phase at about 150.degree. F. over about 41/2 hours. After polymerization is completed a post-cook-treatment of about 3 hours may be used to reduce the free monomer and to add the neutralizing agent to the latex composition. The buffering, using neutralizing materials, to pH range of 6-8 provides, a storage stable of one component web saturant capable of being dried up to temperature of about 180.degree. F. .+-. 10.degree. F. to produce thermoplastic intermediate stock material that has thermoset properties upon being subjected to a heat forming and molding operation.

I have found it necessary to use the "seed" latex technique described above in order to obtain a commercially viable product. The seed latex method with continuous emulsifier addition must be used to obtain a uniform product having good particle size distribution, and stability necessary for a one package cross-linking latex saturant having a minimum shelf-life of at least 1 year.

Using the polymerization process described above I have found it necessary to limit the amount of cross-linking agent N-methylolacrylamide to 6% or less. When more than 6% N-methylolacrylamide is added to the monomer phase coagulation in the latex occurs giving a lumpy saturant (having golf balls size lumps) that cannot be evenly distributed in and on the web. At least about 0.5% N-methylolacrylamide is required to provide a thermoplastic intermediate stockmaterial that will provide sufficient rigidity upon being thermoset in the molding and forming process.

While I do not want to be bound by theoretical considerations it is believed that two critical components provide the novelty of the inventive compositions herein. These components are the N-methylolacrylamide which provides the cross-linking back bone to the latex material and the buffering action of the neutralizing agent. I have found other cross-linking monomers such as N-(isobutoxy methyl) acrylamide may be used. However webs saturated with a N-(isobutoxy methyl) acrylamide modified latex require higher heat activation to begin the cross-linking reaction and require longer dwell times in the molding operation and thus the impregnated webs are not commercially viable.

The neutralizing agents used in the final step of the preparation of the one package composition have the characteristic of adjusting the pH value from the as manufactured value to a pH range of 6.0-8.0. Further, the neutralizing agent is characterized to the extent that it, in combination with N-methylolacrylamide, inhibits premature cross-linking during storage of the latex composition and the drying of the saturated web yet does not interfer with the cross-linking mechanism during the later molding and forming operations. As used herein the term neutralizing agent means any base or buffer that does not interfer with the cross-linking reaction at molding and forming temperatures as hereinafter discussed. Preferably the neutralizing agent is volatile.

Neutralizing agents that have found utility in this invention include ammonium hydroxide, sodium hydroxide, potassium hydroxide, morpholine, methylamine and dimethylamine. The preferred neutralizing agent is ammonium hydroxide because of its volatility and relatively low cost.

Accelerated heat ageing tests have indicated a minimum of a one year shelf-like for the latex composition of this invention.

The first monomer, i.e. styrene, vinylidene chloride, methylmethacrylate, butylmethacrylate, and mixtures thereof, is selected to impart rigidity, hardness and chemical resistance to the final molded product. The second monomer component, i.e., methylacrylate, ethylacrylate, butylacrylate, propylacrylate, 2-ethylhexylacrylate and mixtures thereof contributes flexibility, color stability and

durability to the cured saturated web. The third principal component, N-methylolacrylamide, provides heat a sensitive cross-linking mechanism to the final product.

For the purpose of illustrating the preferred embodiment of the invention reference will be made to a specific manufacture and end use of the product. The examples that follow therefore are not to be construed in a limiting connotation since the latex composition and products made therefrom will find application in many industries.

EXAMPLE 1

A modified latex resin saturant having the following ingredients is prepared as described below:

	PARTS BY WEIGHT
MONOMER PHASE	
Styrene	59.0
Ethylacrylate	41.0
N-Methylolacrylamide	2.0
Water (contained in N-methylolacrylamide)	1.3
Isopropyl alcohol	2.2
AQUEOUS PHASE	
Dimineralized water	79.5
Seed latex 600A.degree. 50% styrene - 50% butadiene	2.1
DOWFAX.sup.(TM) 2A-1 (sodium dodecyldiphenyl ether disulfonate)	0.4
Sodium dodecylbenzene sulfonate	2.2
Potassium persulfate	1.0

The reaction vessel was charged with the seed latex, water and a portion of the emulsifier DOWFAX 2A-1. The reactor was then purged with nitrogen for about 30 minutes and the temperature of the reaction mixture in vessel raised to 150.degree. F. .+-. 1.degree. F. (66.degree. C.). A portion of the potassium persulfate initiator was then added to the reaction vessel. For the next 41/2 hours the monomer phase and the remaining portion of the aqueous phase including the initiator and emulsifiers were added continuously through separate feed streams into the agitated reaction mixture being maintained at 150.degree. F. .+-. 1.degree. F.

The reaction mixture was maintained at 150.degree. F. (66.degree. C.) for approximately three hours following monomer and emulsifier addition. During this time, 0.02 part tertiarybutylhydroperoxide and 0.01 parts isoasborbic acid were added to control the odor and to reduce free monomer content of the latex. The pH value of the finish latex composition was adjusted with ammonium hydroxide to 7.0-8.0 and the total solids content regulated to 50-52%.

EXAMPLE 2

Six 8 .times. 8 inch sheets of non-woven polyester web were saturated with the cross-linking

CDD12530

composition prepared in Example 1, squeeze rolled, dried for 15 minutes at 180.degree. F. following by pressing at 28-30 lbs. in..sup.2 for 15 seconds at 180.degree. F. Sheets prepared in this manner when immersed in acetone were observed. Swelling and softening indicating that cross-linking did not occur. Sheets prepared in this manner were then additionally exposed to heat i.e. 240.degree. F., for 5 minutes. After cooling, the sheets were immersed in acetone. Observation of the sheets showed that they remained stiff and did not swell indicating that cross-linking reaction had taken place.

EXAMPLE 3

In a coating trial non-woven polyester web was unwound from a reel and fed into a coating pan containing the latex composition. The latex composition prepared as in Example 1 contained 50-52% solids. The non-woven web moved through a coating pan at approximately 15-18 ft/min. The latex saturated sheet went into a vertical tower dryer located 3-4 feet above the saturation pan and then into a second dryer and finally to the wind-up stand. The dryer temperatures were set at about 230.degree. so that the web exited from the second dryer with a surface drying temperature of 180.degree. F.

The saturated wound-up sheet was removed from the wind-up stand and samples of the material cut for evaluation. The samples were formed into box toes and counter parts by molding and forming at temperatures between 250.degree.-275.degree. F. The molding and forming step resulted in cross-linking taking place providing a stiff-rigid material useable in manufacturing shoes.

EXAMPLE 4

To determine proper drying conditions six different weight non-woven polyester webs were saturated with a latex cross-linking type web saturant made from monomers containing 59% styrene, 41% ethylacrylate, and 2%, based upon the weight of the monomers, N-methylolacrylamide. The latex was coated as received at 50.1% total solids an as made pH value of 2.6.

The Table below shows the results of a trial run.

Solubility Test in Acetone

WEB	A	B	C	D	F.sup.c	G.sup. c
As Received from Coater	S-F.sup.a	S-F	S-F	S-F	S-R.sup.b	S-R
10 Minutes Cure at 125.degree. C (263.degree. F) Forced draft oven	S-R	S-R	S-R	S-R	S-R	S-R

.sup.a S-F, indicates soft-flexible, no cross-linking has occurred.
.sup.b S-R, indicates stiff-rigid, cross-linking as taken place.
.sup.c Webs F and G were cross-linked during saturation and drying.

The webs decrease in weight per unit area from A to G. F and G, the lightest weight webs, cross-linked during the initial saturation and drying steps. This indicates that the latex, in order to prevent premature cross-linking should have been neutralized prior to the web saturation step.

EXAMPLE 5

Five rolls of non-woven polyester web were saturated as described in Example 3 with a neutralized latex cross-linking type saturant prepared as described in Example 1. The temperatures of both the tower and the tunnel dryers were controlled so that the saturated web exited at 180.degree. F. from the tunnel dryer. Samples were periodically taken from the saturated and dried webs and checked for cross-linking. All samples were acetone swellable indicating that no cross-linking has taken place in any of the different webs.

Additional samples were subjected to 250.degree.-275.degree. F., cure for 3-5 minutes and then rechecked for cross-linking. All samples were acetone insoluble indicating that cross-linking had taken place. The amount of latex saturant consumed indicated that an average coating was approximately 13.5 ounces per square yards.

EXAMPLE 6

Following the procedure set forth in Example 1 a reaction vessel with an aqueous phase containing seed latex and a portion of a emulsifier, and an initiator is prepared and heated to about 150.degree. F. A monomer mixture of 59 parts vinylidene chloride, 41 parts butylacrylate, and 2 parts N-methylolacrylamide, 2.2 parts isopropyl alcohol and the remaining initiator and emulsifiers may be added to the aqueous phase at 150.degree. .+-. 1.degree. F. continuously over a period of 41/2 hours to complete the polymerization. The as manufactured pH of the latex composition may then be buffered to between 6.0-8.0 with a neutralizing agent selected from ammonium hydroxide, sodium hydroxide, potassium hydroxide, morpholine and mixtures thereof.

When the buffered latex is saturated on non-woven fibrous materials the saturated materials may be dried up to about 180.degree. F. without cross-linking taking place.

EXAMPLE 7

In a manner similar to that described in Example 6 a buffered latex cross-linking saturant may be manufactured from a monomer mixture containing 59 parts methylmethacrylate, 41 parts methylacrylate, and 2 parts N-methylolacrylamide. After polymerization and neutralizing the cross-linking may be applied as described above and dried as described above without initating the cross-linking mechanism.

Having described the essence of my invention it is evident that many variations can be effected without departing from the limit of the invention as defined in the appended claims.

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(1 of 1)

United States Patent *4,182,649*
Isgur , et al. *** January 8, 1980**

Polyurethane foam sheet and method

Abstract

Disclosed herein is a composite, self-supporting, polyurethane foam sheet prepared by forming an aqueous dispersion of hydrophilic polyurethane foam particles with fibers to serve as a binder therefor, wet-layering the dispersion onto a supporting screen to form a sheet, and removing water from the sheet. If desired, a porous web, woven or non-woven, e.g. paper, cloth, etc., can be positioned on the screen with the dispersion being layered out onto the web to form a laminar composite structure. Whether in sheet form or as a laminar structure the product of the invention is formed rapidly and possesses a desirable soft or cushioning feel.

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[*] Notice: The portion of the term of this patent subsequent to August 29, 1995 has been disclaimed.
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CDD12534

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Parent Case Text

This application is a continuation-in-part of Ser. No. 656,674 filed Feb. 9, 1976 and entitled, "Foam Sheet and Method", now U.S. Pat. No. 4,110,508.

Claims

What is claimed is:

1. A method for preparing a compressible, resilient, homogenous composite sheet having sufficiently low modulus of compression to provide a cushioning effect, said method comprising

(A) forming an aqueous dispersion of fibers,

(B) forming an aqueous dispersion of particles of hydrophilic polyurethane foam prepared by dispersing a prepolymer of a hydrophilic oxyalkylene polyol capped with an isocyanate in water and allowing the isocyanate groups to react essentially simultaneously with the water to form polyurethane particles in-situ, wherein said prepolymer is from about 10 to about 60% by weight, based on total weight of prepolymer and fibers, wherein said polyol has a molecular weight from about 200 to about 20,000 and contains at least 50 mole percent oxyethylene units, wherein the size of the polyurethane particles are not less than about 0.01 inch mesh, and wherein from about 7 to about 50 parts of water is used for every part of prepolymer,

(C) mixing dispersion (A) and (B),

(D) wet-layering the mixed dispersion onto a support, and

(E) removing water from the resulting supported fiber/foam sheet.

2. A method as in claim 1 wherein the fibers are asbestos.

3. A method as in claim 1 wherein cellulosic fibers are employed.

4. A method as in claim 1 wherein latex is added to the mixed dispersions before wet layering.

5. A method as in claim 1 wherein the hydrophilic oxyalkylene polyol contain at least 60 mole percent

CDD12535

of oxyethylene units in the backbone.

6. A method as in claim 1 wherein from about 7 to about 50 parts of water is used for every part of isocyanate capped prepolymer.

7. A method for preparing a compressible resilient, homogeneous compsite sheet having sufficiently low modulus of compression to provide a cushioning effect, said method comprising:

(A) forming an aqueous dispersion of fibers and particles of hydrophilic polyurethane foam by dispersing into an aqueous fiber dispersion a hydrophilic oxyalkylene polyol capped with an isocyanate whereby said capped polyol reacts essentially simultaneously with the water in said fiber dispersion to form particulate polyurethane foam particles in-situ to produce a fiber/foam dispersion, wherein said capped polyol is from about 10 to about 60% by weight based on total weight of capped polyol and fiber, wherein said polyol has a molecular weight from about 200 to about 20,000, wherein said polyol contains at least about 50 mole percent oxyethylene units, wherein the foam particles size is not less than about 0.01 inch mesh, and wherein from about 7 to about 50 parts of water for every part of capped polyol is employed.

(B) wet-layering said fiber/foam dispersion onto a support, and

(C) removing water from the resulting supported fiber/foam sheet.

8. A method as in claim 7 wherein the fibers are asbestos.

9. A method as in claim 7 wherein cellulosic fibers are employed.

10. A method as in claim 7 wherein latex is added to the dispersion before wet layering.

11. A method as in claim 7 wherein the hydrophilic oxyalkylene polyol contains at least 60 mole percent of oxyalkylene units in the backbone.

12. A method as in claim 7 wherein at least 7 parts of water is used for each part by weight of the combined weight of capped polyol and fiber.

13. In the method for preparing a compressible resilient, homogenous composite sheet by forming an aqueous dispersion containing particulate foam and fibers, wet-layering the fiber/foam dispersion onto a support to form a sheet, and removing water from the resulting supported sheet, the improvement comprising using, in place of shredded foam particles, a particulate dispersion of polyurethane foam prepared by dispersing an isocyanate-capped hydrophilic polyoxyalkylene polyol in water and allowing the isocyanate groups to react essentially simultaneously in-situ with the water to provide the foam particles, wherein said capped polyol is from about 10 to about 60% by weight based on total weight of capped polyol and fibers, wherein said hydrophilic polyoxyalkylene polyol has a molecular weight from about 200 to about 20,00 and contains at least 50 mole percent oxyethylene units, wherein the size of said foam particles is not less than about 0.01 inch mesh, and wherein from about 7 to about 50 parts of water is used for every part of capped polyol.

14. A method as in claim 13 wherein a separate fiber dispersion and a separate particulate foam dispersion are formed and subsequently combined to form the fiber/foam dispersion.

15. A method as in claim 14 wherein the fibers are asbestos.

CDD12536

16. The method as in claim 14 wherein cellulosic fibers are employed.

17. A method as in claim 16 wherein latex is added to the dispersion of cellulosic fibers.

18. A method as in claim 14 wherein the hydrophilic oxyalkylene polyol contains at least 60 mole percent of oxyethylene units in the backbone.

19. A method as in claim 13 wherein the hydrophilic isocyanate-capped prepolymer is dispersed in an aqueous dispersion of fibers to form the fiber/foam dispersion.

20. A method as in claim 19 wherein the fibers are asbestos.

21. A method as in claim 19 wherein cellulosic fibers are employed.

22. A method as in claim 19 wherein latex is added to the fiber/foam dispersion before wet-layering.

23. A method as in claim 19 wherein the hydrophilic oxyalkylene polyol contains at least 60 mole percent of oxyethylene units in the backbone.

24. A compressible, resilient, homogenous composite sheet comprising in combination, particles of hydrophilic polyoxyalkylene polyurethane foam and fibers interwined therewith and binding the particles together to form said sheet, the improvement wherein said foam particles are formed by in-situ foaming by dispersing an isocyanate capped hydrophilic oxyalkylene polyol in an aqueous dispersion of fibers, according to the method of claim 12.

25. A sheet as in claim 24 wherein the fibers are asbestos.

26. A sheet as in claim 24 wherein cellulosic fibers are employed.

27. A sheet as in claim 24 wherein latex is employed in combination with the fibers.

28. A sheet as in claim 24 wherein the oxyalkylene polyurethane contains at least 50 mole percent of oxyethylene units in the backbone.

29. A composite laminate comprising in combination, particles of hydrophilic polyoxyalkylene polyurethane foam and fibers intertwined therewith and binding the particles together to form a sheet, and a porous web supporting and adhering to said sheet, the improvement wherein said foam particles are formed by in-situ foaming by dispersing an isocyanate capped hydrophilic oxyalkylene polyol in an aqueous dispersion of fibers according to the method of claim 12.

30. A laminate as in claim 29 wherein the web is a woven fabric.

31. A laminate as in claim 29 wherein the web is a non-woven material.

32. A laminate as in claim 29 wherein the fibers are asbestos.

33. A laminate as in claim 29 wherein the fibers are cellulose.

34. A laminate as in claim 29 wherein latex is employed in combination with the fibers.

35. A laminate as in claim 29 wherein the polyurethane foam particles contain at least 60 mole percent

oxyethylene units in the polyoxyalkylene backbone.

Description

BACKGROUND OF THE INVENTION

Numerous attempts have been made to rapidly form foam materials into sheets which are homogeneous while possessing structural strength and also retaining the cushioning effect of the foam. For example, "one-shot" procedures for rapidly building up a sheet of polyurethane foam using spray techniques are well known. For many applications it is desirable to incorporate fibers into the polymer mixture.

In U.S. Pat. No. 4,110,508 referred to above a procedure for incorporating fibers is described. In this application hydrophilic polyurethane prepolymer is foamed and the resulting foam is shredded. Subsequently the shredded foam is dispersed in combination with fibers (e.g. asbestos or wood pulp) into water and the resulting aqueous dispersion is wet-layered onto a support which can be a screen or fabric web.

The present invention is an alternate and superior method for preparing the sheets and sheet/fabric laminates described in U.S. Pat. No. 4,110,508, said application being expressly incorporated by reference into the present application to the extent U.S. Pat. No. 4,110,508 describes the urethane prepolymer employed, the method of foaming and shredding the foam to produce hydrophilic particles, the preparation of sheets and laminates and describes these products and their utilities.

The present invention is an improvement over the invention of U.S. Pat. No. 4,110,508 in that the separate steps of foaming and shredding the resulting foam are avoided. By use of the present invention a hydrophilic urethane prepolymer is dispersed in water and foamed simultaneously which results in a simplified process as well as a savings in time. Also it is possible to add the prepolymer directly to an aqueous dispersion of fibers to form a sheet having improved homogeneity. In this instance, sheets having improved tensile strength can be obtained.

DESCRIPTION OF THE INVENTION

The present invention is a compressible, resilient, homogeneous composite sheet comprising in combination, particles of hydrophilic polyoxyalkylene polyurethane foam and fibers intertwined therewith and binding the foam particles together to form a homogeneous sheet. By homogeneity it is meant that the texture of the sheet is generally uniform in terms of strength and appearance. As an indication of compressibility and resiliency it has been found that the indentation range at 25% compression of the sheet was from about 0.5 to about 200. After one minute relaxation the range was from about 0.5 to about 250.

Where asbestos fibers are employed the indentation range for sheets of the invention is from about 25 to about 200. For cellulosic fibers the range is from about 0.5 to about 5.3. Sheets of the invention using cellulose fibers also exhibit excellent water absorption and vapor transmission. Water absorption is generally at least 350 weight percent based on the weight of sheets at normal room temperature and humidity, e.g. 40%.

In determining indentation range ASTM D-1564 was employed with a rate of compression equal to 0.1 inch/minute at a temperature of 23.degree. C. and 50% R.H. The samples were not conditioned for any length of time prior to testing.

CDD12538

The compressible composite sheet of the invention is prepared by forming an aqueous dispersion of fibers and particles of hydrophilic polyurethane foam. The particles are formed by dispersing a hydrophilic oxyalkylene polyol capped with an isocyanate in water and allowing the isocyanate groups to react with the water to form a particulate dispersion of polyurethane foam particles. When adding the prepolymer it is desirable to agitate the water. The method of agitation is not critical. For example, a common laboratory mixer can be employed. It has been found that in the resulting dispersion the foam particles have a generally uniform size of less than about 0.08 inch and preferably from about 0.03 inch to about 0.01 inch. In forming the dispersion, a surfactant can be employed. However, it has been found that the foam particle size may be undesirably small, i.e. less than 0.01 inch. To avoid this situation, a different surfactant can be used, or the dispersion can be formed without using a surfactant.

It has been found that the dispersion of fibers and foam particles can be formed in several ways. First an aqueous dispersion of foam particles can be formed as described above. This aqueous dispersion can then be combined with an aqueous dispersion of the fibers using suitable agitation so that the foam particles and fibers are uniformly dispersed. Secondly (and preferably) the isocyanate-capped prepolymer can be added with agitation, directly into a dispersion of fibers. It has been found that by using direct agitation, the resulting sheet is more homogeneous. Also the separate processing step of forming an aqueous dispersion of the prepolymer is eliminated. For these reasons the direct addition procedure is preferable.

The steps of applying the aqueous fiber/foam dispersion to a supporting screen or other surface and removing water from the resulting sheet-like product can be carried out using well-known paper making techniques. For example, for small-scale applications the aqueous fiber/foam dispersion can be placed in a Williams pulp testing apparatus. The dispersion will be positioned on the screen and the water phase will drain through the screen and be removed. Subsequently the resulting sheet can be further dried as desired. For large-scale applications the fiber/foam dispersion can be placed in the headbox of a standard Fordrinier machine and dispersed onto a screen. Using this method the sheet can be rapidly formed in large quantities. The aqueous phase drains from the sheet and subsequently the sheet can be dried further.

The binding fibers employed in the present invention include materials such as asbestos, wood pulp or other similar materials dispersible in water. The length or size of the fibers is not critical. Very small fibers, e.g. less than 1/4 inch would not exert adequate binding action and fibers larger than about 1 inch would tend to make dispersion in water and other processing steps difficult. However, use of surfactants or suitable agitation methods could be employed to extend the range of fibers usable in the invention. Other types of fibers useful include glass fibers, polyester fibers, olefinic fibers and polyamide fibers. It has been found that not all fibers, e.g. polyester fibers are useful in every application, i.e. the homogeneity or structural strength of the sheet may be impaired. For example polyester fibers should not be used as the sole binding fiber. It is necessary to add cellulose, asbestos or other types of fibers to increase the binding efficiency of the polyester. The binding efficiency of the fibers can also be increased by using any of the suitable, conventional, binding-type latexes, e.g. SBR, vinyl acetate or acrylic latex.

As well known in the art, another factor tending to increase fiber efficiency in binder applications is "beating" or fibrillation to unravel the ends of individual fibers or packets of fibers. This technique is especially useful with cellulosic fibers. Such fibers can be employed advantageously in the present invention.

As is well known in the art, where a cationic fiber such as asbestos is employed an anionic latex will precipitate and be effective. However, where an anionic fiber such as wood pulp is employed, it is

necessary to add alum or a similar material to precipitate the latex. Where employed, the latex can be added at any convenient step, e.g. the latex can be added to an aqueous dispersion of fibers prior to adding the prepolymer or foam particles. Alternatively the latex can be added following formation of the fiber/foam dispersion.

In forming the fiber/foam dispersion the amount of prepolymer employed will be from about 10 to 60 weight percent based on the total weight of the prepolymer and fibers, but excluding water. The fibers should be from 90 to 40 weight percent using the same basis. Where a latex is employed the amount of latex should be from about 4 to 10 weight percent based on the total weight of prepolymer, fibers and latex..sup.1/ Within the above ranges it has been found that increasing the amount of prepolymer increases the "softness" or cushioning effect of the resulting sheet but tends to reduce the tensile strength of the sheet. Increasing the amount of fibers employed tends to increase the strength of the sheet but reduce the cushioning effect. Within the above ranges it may also be possible to increase the strength of the sheet and still retain a high degree of softness by dispersing the prepolymer directly in the aqueous dispersion of fibers according to the second method described above. Given the relatively narrow range of ingredients described, it can be easily determined by a series of test runs whether direct addition of the prepolymer is advantageous in view of the particular fiber and other processing conditions employed.

.sup.1/ Higher amounts of latex can be employed but this results in more "rubbery-like" properties in the finished sheet or inefficient use of the latex polymer.

In another embodiment of the invention the fiber/foam dispersion can be wet-layered onto a porous web such as cloth or a non-woven material. Using the Williams apparatus it is possible to position the fabric over the screen. Suction can be applied to facilitate drainage of the water. It has been found that the foam fiber sheet bonds to the fabric to form a laminar structure. For large-scale applications a Fordrinier machine can be modified to insert fabric over the supporting screen so that the fiber/foam dispersion emptying from the headbox is positioned directly on the fabric in sheet-like form. This procedure results in a relatively fast method of providing a soft backing to fabric. To increase binding of the fiber/foam sheet to the fabric, it is desirable to incorporate a latex into the dispersion as described previously.

In preparing dispersions useful in the present invention (foam dispersion--fiber dispersion--fiber/foam dispersion) the amount of water employed is not critical. The water level should be sufficient to permit processing of the dispersions, e.g. if the water level is too low in the foam or fiber dispersions it will be difficult to properly disperse the solid phase and the resulting dispersion will encounter separation problems as well as possess an undesirably high viscosity. Where prepolymer is being dispersed in water (with or without fibers), from 7 to 50 parts of water for every part of prepolymer should be employed. In the finished fiber/foam dispersion at least 7 parts of water should be employed for each part by weight of the combined weight of prepolymer and fiber. In forming dispersions the upper limit on the amount of water employed is not critical with the primary consideration being ease of processing, e.g. because water must be removed from the finished sheet, it is desirable to avoid using more water than necessary in dispersing the materials.

Hydrophilic Oxyalkylene Polyurethane Foam

The invention utilizes polyether polyurethanes, i.e. the branch-points of the foam are connected by essentially linear polyoxyalkylene chains. The foam is hydrophilic which means that at least 50 mole percent of the oxyalkylene units (excluding any initiators at branch-points) are oxyethylene units with the balance being oxypropylene, oxybutylene or other oxyalkylene units. Hydrophilic foams are utilized in the present invention to insure that the foam particles can be dispersed in water. To promote dispersion in polyethers where the oxyethylene content approaches 60% or so (e.g. from about 60 to 75

CDD12540

mole percent) it may be desirable to use a surfactant such as those specified earlier.

The hydrophilic foam can be made by any of the common processes such as the "one-shot", prepolymer or quasi-prepolymer processes. After the foam is prepared it can be shredded and used as described in U.S. Pat. No. 4,110,508.

For purposes of the present invention it is preferred to use the prepolymer technique in preparing the hydrophilic foam particles thereby avoiding separate foaming and shredding steps. Suitable prepolymers are prepared by capping a polyoxyalkylene polyol with an excess of polyisocyanate, e.g. toluene diisocyanate. Prior to capping the polyol should have a molecular weight of from about 200 to about 20,000, and preferably from about 600 to about 6,000. The hydroxy functionality of the polyol and the corresponding isocyanate functionality following capping is from 2 to about 8. If foams are formed from prepolymers with an isocyanate functionality of about 2 the resulting foam is essentially linear and does not have as much tensile strength as crosslinked foams. Accordingly, if the isocyanate functionality is about 2 a crosslinker can be employed although the linear non-crosslinked foams are operable in the present invention, i.e. the foam particles can be dispersed in water and layered out to form a sheet. Suitable crosslinkers are well known in the polyurethane art and include by way of example tolylene-2,4,6-triamine, ethylene diamine, diethanolamine, diethylenetriamine, triethylene-tetramine, tetraethylenepentamine, and ethanolamine.

Examples of suitable polyols (to be capped with polyisocyanates) include: (A) essentially linear polyols formed for example by reaction of ethylene oxide with ethylene glycol as an initiator. As discussed above mixtures of ethylene oxide with other alkylene oxides can be employed as long as the mole percent of ethylene oxide is at least 60 percent. Also as stated, it may be desirable to use crosslinkers with these systems in which case the crosslinker can be included in the water into which the prepolymer is dispersed. Where the linear polyethers are mixtures of ethylene oxide with, e.g. propylene oxide, the polymer can be either random or a block copolymer and the terminal units can be either oxyethylene or oxypropylene. A second class of polyol (B) includes those with a hydroxy functionality of 3 or more. Such polyols are commonly formed by reacting alkylene oxides with a polyfunctional initiator such as trimethylolpropane, pentaerythritol, etc. In forming the polyol B, the alkylene oxide used can be ethylene oxide or mixtures of ethylene oxide with other alkylene oxides as described above. Useful polyols can be further exemplified by (C) linear branched polyfunctional polyols as exemplified in A and B above together with an initiator or crosslinker. A specific example of C is a mixture of polyethylene glycol (m. w. about 1,000) with trimethylolpropane, trimethylolethane or glycerine. This mixture can be subsequently reacted with excess polyisocyanate to provide a prepolymer useful in the invention. Alternatively the linear or branched polyols, (e.g. polyethylene glycol) can be reacted separately with excess polyisocyanate. The initiator, e.g. trimethylolpropane, can also be separately reacted with polyisocyanate. Subsequently the two capped materials can be combined to form the prepolymer.

Suitable polyisocyanates useful in preparing prepolymers include toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, commercial mixtures of toluene-2,4- and 2,6-diisocyanates, ethylene diisocyanate, ethylidene diisocyanate, propylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate, m-phenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,6-hexamethylenediisocyanate, 1,4-tetramethylene-diisocyanate, 1,10-decamethylenediisocyanate, 1,5-naphthalenediisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-phenylenediisocyanate, 4-chloro-1,3-phenylenediisocyanate, 4-bromo-1,3-phenylenediisocyanate, 4-ethoxy-1,3-phenylenediisocyanate, 2,4'-diisocyanatodiphenylether, 5,6-dimethyl-1,3-phenylenediisocyanate, 2,4-dimethyl-1,3-phenylenediisocyanate, 4,4'-diisocyanatodiphenylether, benzidinediisocyanate, 4,6-dimethyl-1,3-phenylenediisocyanate, 9,10-anthracenediisocyanate, 4,4'-diisocyanatodibenzyl, 3,3'-dimethyl-4,4'-

diisocyanatodiphenylmethane, 2,6-dimethyl-4,4'-diisocyanatodiphenyl, 2,4-diisocyanatostilbene, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 1,4-anthracenediisocyanate, 2,5-fluorenediisocyanate, 1,8-naphthalenediisocyanate, 2,6-diisocyanatobenzfuran, 2,4,6-toluenetriisocyanate, and p,p',p"-triphenylmethane triisocyanate.

Suitable initiators useful in preparing prepolymers include propylene glycol, trimethylene glycol, 1,2-butylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,2-hexylene glycol, 1,10-decanediol, 1,2-cyclohexanediol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 4-methyl-3-cyclohexene-1,1-dimethanol, 3-methylene-1,5-pentanediol, diethylene glycol, 1,2,6-hexanetriol, 1,1,1-trimethylolpropane, 3-(2-hydroxyethoxy)-1,2-propanediol, 3-(2-hydroxypropoxy)-1,2-propanediol, 2,4-dimethyl-2-(2-hydroxyethoxy)methylpentanediol-1,5, 1,1,1-tris[(2-hydroxyethoxy)methyl]ethane, 1,1,1-tris[(2-hydroxypropoxy)methyl]propane, triethanolamine, triisopropanolamine, resorcinol, pyrogallol, phloroglucinol, hydroquinone, 4,6-di-tertiarybutyl catechol, catechol, and orcinol.

Use of Additional Materials

Because of the relatively large amount of water used in forming the various dispersions it is possible to combine other materials into the finished sheet. This option is generally not available with systems using a limited amount of water. Useful additives to the water include crosslinkers (especially where the prepolymer is essentially linear), flame retardants, antistats, soil repellents, fungicides, insecticides, stabilizers, fillers, biostats, color additives, organic solvents, blowing agents, dispersing agents, resins, etc. By homogeneously distributing these materials in the aqueous portion of the dispersion, it is possible to distribute the additives widely and uniformly throughout the finished sheet product.

Useful illustrative examples of materials which may be added include porous structures such as particulate wood fibers; rock wool; glass wool; bagasse; straw; cork; sponge rubber; foamed polystryene; and the like.

Fire or flame retardant additives usefully included alone or in combination in the aqueous reactant are represented by, for example, zinc borate; calcium carbonate; alum; ferrous sulfate; borax; melamine and boric acid; melamine phosphate; ammonium phosphate; stannic oxide; ammonium sulfate; ammonium sulfamate; titanium and antimon oxides in combination with halide materials and in particular the oxychlorides; aluminum hydrate; ceric hydrate; tetrakis (hydroxymethyl) phosphonium chloride; bromoform and triallyl phosphate; phosphoroxytriamide; chlorinated paraffins; tris (2-ethyl hexyl) phosphate; tris (2,3-dibromopropyl) phosphate, triphenyl phosphate, cresyl diphenyl phosphate; and the like.

The sheet-like materials of the invention retain dimensional stability during wetting and drying cycles and for functional, reinforcing, strengthening, binding, opacifying or cushioning effects; they are useful for various end products such as drapery backing, upholstery backing, blankets, absorptive padding, wall coverings, acoustical panels, protective and/or fire retardant surfaces, apparel, shoe linings, separation membranes, filters and the like. The feature of water vapor permeability of sponges resulting from the hydrophilic nature of the polyoxyethylene polyol reactant renders them attractive for apparel. These present materials are also useful as leather substitutes.

The following examples are presented to illustrate the invention. Examples 1-11 deal with preparation of hydrophilic foams, shredding the foams, dispersing the foam particles in water, and wet-layering the particles to form a sheet. Examples 14-28 deal with formation of foam particles by dispersing a prepolymer into water or an aqueous fiber dispersion followed by wet-layering to form a sheet. Examples 12 and 13 describe prepolymers useful in forming sheets either by the shredding process or by dispersion of the prepolymer into water to provide the foam particles.

CDD12542

EXAMPLE 1

To a reaction vessel containing 3,092 grams, representing 1 mole, 3 eq. OH, of a triol prepared from potassium hydroxide catalyzed reaction of 92 grams anhydrous glycerol with 3300 grams of ethylene oxide, were added 522 grams, representing 3 moles, 6 eq. NCO of tolylene diisocyanate having about 80/20 mixture of 2,4 isomer/2,6 isomer. The reaction exotherm was kept at 70.degree. C. by external cooling with water, while stirring for 4 hours. The actual isocyanate content, determined by titration with standard n-butylamine solution in toluene, remained at the constant level of 0.79 meq. NCO/gram relative to a theoretical content of 0.83 meq. NCO/gram. The resultant pale yellow syrup was found to solidify at about 30.degree.-35.degree. C., was soluble in toluene, and acetone, readily reacts with water, and had the following average formula: ##STR1## where n has an average value of about 22. The theoretical molecular weight of the resin product is about 3615.

200 grams of the capped resin having an eq. NCO content of 0.016 was stirred briefly and reacted with 200 grams water. The moles H.sub.2 O/NCO groups was 73.2. The reaction mixture was immediately foamed, shredded mechanically to an average particle size to pass through a wire screen of 0.030 inch mesh and wet layered using the paper pulp technique to prepare a bound foam fabric having a thickness when dry of about 0.125 inches. The hydrophilic product was found to have good breathability and comfort characteristics and excellent moisture equilibrium maintenance.

EXAMPLE 2

To a reaction vessel containing 4,136 grams, representing 1 mole, 4 eq. OH, of a tetrol prepared from sodium methoxide catalyzed reaction of 136 grams pentaerythritol with 4400 grams of ethylene oxide, were added 696 grams of tolylene diisocyanate having about 80/20 mixture of 2,4 isomer/2,6 isomer. The reaction was carried out using the procedure of Example 1. The actual isocyanate content noted was 0.86 meq. NCO/gram relative to a theoretical content of 0.83 meq. NCO/gram. The recovered product was a colorless syrup which solidified at about 35.degree.-40.degree. C., was soluble in toluene and acetone, readily reacts with water, and had the idealized average formula: ##STR2## where n has an average value of about 22. The theoretical molecular weight of the resin product is about 4832.

50 grams, of the recovered capped resin product from this example, were reacted with 55 grams water. The moles H.sub.2 O/NCO groups was about 73.2. The foam product was shredded, combined with 7.5 grams cellulosic pulp and 20 grams of acrylic latex. These ingredients were wet layered. Corresponding results to that of Example 1 were realized. It was further noted that the hydrophilic polyurethane interpenetrated the fibers of the fabric and served as a reinforcing binder. The fabric remained soft and pliable.

EXAMPLE 3

A solution of 92 grams glycerol and 1000 grams of polyoxyethylene (1000) glycol was outgassed at 100.degree. C. and 10 Torr for two hours. To the outgassed solution was added 870 grams tolylene diisocyanate having an 80/20 mixture of 2,4 isomer/2,6 isomer. The reaction solution was stirred at 60.degree. C. for four hours whereupon the actual isocyanate content reached a constant 2.49 meq. NCO/gram relative to a theoretical content of 2.54. 31.3 parts of the resin product had a theoretical molecular weight of 615.

20 grams of water containing 0.5 grams of antimony trioxide and 5 grams of polyvinyl chloride-latex particles was mixed with 10 grams of the capped resin product having an eq. NCO content of 0.016. The moles H.sub.2 O/NCO groups was 125. The foam so generated was shredded and layered onto a fabric

CDD12543

by the procedure of Example 1. The composite product was found to have excellent comfort, fire retardancy and moisture equilibrium maintenance.

EXAMPLE 4

The procedure of Example 1 was repeated except that 20 grams of the shredded product was combined with 20 grams of water and 1.5% by weight soft wood paper pulp. The product was characterized with a soft open cell structure which was flexible yet fairly tough and was found to have excellent properties. The weight of pulp employed is based on the weight of the foam particles.

EXAMPLE 5

In order to demonstrate use of polyoxyethylene polyisocyanate in making products with attractive colors, a 10 gram portion of the polyoxyethylene tetraisocyanate prepared in Example 2 was mixed with 10 grams of water containing 0.5 gram of Hansa yellow color. A composite having a yellow color and the excellent characteristics of the product of Example 2 resulted.

EXAMPLE 6

In order to demonstrate capping of a polyoxyethylene diol with a polyisocyanate having a functionality greater than 2, to give polyisocyanate foams with higher crosslink density and superior physical properties, lower solubility, and greater hydrolytic stability than products from polyoxyethylene diisocyanates, a 1000 gram portion, of polyoxyethylene glycol of 4000 weight average molecular weight was outgassed at 110.degree. C. and 10 Torr for two hours. Next, to this outgassed liquid was added at 60.degree. C. 200 grams, of polymethylene polyphenylisocyanate commercially available under the name PAPI 901 by Upjohn Co. This latter material has nearly three isocyanate groups per molecule and an isocyanate equivalent weight of 133. A dark reaction solution was noted which was stirred at 60.degree. C. to 70.degree. C. for five hours whereupon the NCO content reached a constant 0.825 meq. NCO/gram relative to a theoretical value of 0.833. The resultant dark product syrup solidified at 45.degree. C. to form a brown, waxy product. Addition of 10 grams of water to 10 grams of the prepared liquid polyisocyanate at 60.degree. C. resulted in a foam and using the procedure of Example 1 gave a resultant tan, soft, flexible, hydrophilic fabric product.

EXAMPLE 7

In order to illustrate use of copolymers of 75% ethylene oxide and 25% propylene oxide along with methylene dicyclohexyl diisocyanate to form a triisocyanate that readily reacts with water to give a hydrophilic product, a mixture of 13.4 grams, 0.1 mole of trimethylolpropane and 0.6 grams, 0.01 mole of potassium hydroxide was stirred at 100.degree.-180.degree. C. in the presence of 250 grams of ethylene oxide at 20 to 100 psi. After 3 hours the reaction pressure dropped to one atmosphere. To the reaction product syrup was then added 250 grams of propylene oxide with stirring at 100.degree.-180.degree. C., and a pressure of 20 to 75 psi for 4 hours whereupon the reaction pressure at 100.degree. C. dropped to one atmosphere. To this reaction product syrup having a brown color was added 500 grams of ethylene oxide. The reaction was stirred at 100.degree.-180.degree. C. for 12 hours whereupon the reaction pressure dropped to one atmosphere at 100.degree. C. The resultant brown oil was stripped of volatiles at 50.degree. to 100.degree. C. at 10 Torr resulting with 978 grams of brown syrup having a hydroxyl content of 0.32 meq. OH/gram relative to 0.31 meq/gram theory.

To 931 grams, 0.30 eq. OH of the prepared triol was added 88.0 grams, 0.32 moles, of dicyclohexylmethane diisocyanate. The solution stirred at 60.degree. C. for 8 hours whereupon the NCO content of the polymer reached a constant 0.33 meq./gram relative to 0.32 theory. The triisocyanate

CDD12544

product was characterized as a light amber syrup having a viscosity of 12,000 cps at 25.degree. C. (Brookfield).

To a 10 gram portion of the above triisocyanate containing 0.1 gram of silicone surfactant L520 by Union Carbide was added with good mixing 12 grams of water. A product having similar properties to those of the product of Example 1 resulted.

EXAMPLE 8

The following substrates were coated on one side by wet layering using the product of Example 3.

Substrate	Size (Cm.)	Average Thickness Foam Pad (mm)
Regular kraft paper	10 .times. 40	4.5
Upholstery fabric, Nylon	10 .times. 40	4.1
Muslin sheet	10 .times. 40	5.5
Unbacked, needled carpet, polypro-pylene fiber, (0.05 g/cm.sup.2 density)	20 .times. 40	4.5
Rayon nonwoven web	10 .times. 40	3.8
Polyethylene nonwoven web	10 .times. 40	3.5

EXAMPLE 9

Sheets were prepared by mixing the shredded foam of Example 1 and additional ingredients as stated in the table below into about 4 liters of water with processing through a "Williams Standard Pulp Testing Apparatus".

Conc. Shredded HYPOL	Pulp	Asbestos	Latex (Solids)	Alum

CDD12545

(g)	Conc. (g)	CSF.sup.(1)	Conc. (g)	Conc. (g)	Conc. (g)	Substrate.sup.(2)
25	25	600	--	--	--	Cheese Cloth
25	5	600	--	8	--	Nonwoven Polyester Web
60	5	600	--	--	--	--
60	10	520	--	--	--	Upholstry Fabric
25	--	--	25	7	0.6	--
50	10	420	--	--	--	--

.sup.(1) Canadian Standard Freeness
.sup.(2) The wire screen of the Pulp Testing Apparatus was covered by the substrate and the foam sheet formed on the substrate during processing. Corresponding results may be realized.

EXAMPLE 10

The procedure of Example 8 was repeated using a 20.times.24 cm. polyamide unbacked carpet except that 30 grams of shredded foam was wet layered.

EXAMPLE 11

The procedure of Example 9 was repeated except that a 10.times.40 inch section of muslin sheet was laminated by wet layering with 15 grams of shredded foam.

A 6 mm thick pad of flexible foam laminate resulted; the muslin fabric being integrally bonded. This product was very absorbent of water and was useful as a wiping cloth; similar in effectiveness to chamois. It is also useful as a fabric interliner for wearing apparel, shoe and boot linings and insoles, various types of gas and liquid filters, light weight blankets, mattress covers, coasters, tablecloths, diapers, incontinent pads, upholstery fabrics, mattress ticking, drapery fabrics, sound absorbing wall coverings, vehicle headlining materials, carpet and rug under padding, bathroom and bedroom slippers and the like.

EXAMPLE 12

A prepolymer is prepared by admixing trimethylolpropane (TMOP) with polyethylene glycol (PEG - 1,000). The mole ratio of PEG/TMOP was 2:1. The polyol mixture was admixed with sufficient toluene diisocyanate (TDI) to react with about 95% of the hydroxyl groups in the polyol. The reaction was carried out at 60.degree. C. Following the capping reaction a second addition of TDI was made sufficient to react with about 15% of the hydroxyl groups originally present in the polyol, thereby providing a 10% excess of TDI. Following the second addition the reaction mixture was maintained at a temperature of about 60.degree. C. for a two-hour period. The resulting prepolymer is referred to below as Prepolymer 1.

EXAMPLE 13

A prepolymer was prepared following the general procedure of Example 12. The PEG/TMOP ratio was 3.33:1 and in the first incremental addition of TDI approximately 93% of theory was employed. In the

second addition 12% of theory was employed. The resulting prepolymer is referred to below as Prepolymer 2.

EXAMPLES 14-28

The following tables (A-C) illustrate the preparation of sheets by dispersion of prepolymer into water to form foam particles. Dispersion is accomplished by slowly pouring the prepolymer into 7 to 50 times its weight of water while stirring with a standard laboratory mixer. The water may contain additional ingredients such as asbestos, wood pulp, or polyester fibers. Examples 19-23 additionally employ latex (GRS - 2,000) and alum. The types of ingredients employed, amounts, and results obtained are set forth in the following tables.

TABLE A

Example	Asbestos.sup.1 %	Prepolymer.sup.1 %	Prepolymer Type	Addition Technique	Sheet App.	Tensile Strength.sup.2
14	51.5	48.5	1	A	Slight Layering	25
15	51.5	48.5	1	B	Almost Homogen.	21
16	51.5	48.5	1	B	Homogen.	39
17	51.5	48.5	2	B	Homogen.	10
18	34.7	65.3	2	B	Homogen.	very weak

A Asbestos and Prepolymer dispersions prepared separately and then mixed.
B Prepolymer dispersed directly into dispersion of asbestos fibers.
.sup.1 The percentages for asbestos fibers and prepolymer are based on th combined weight of fibers plus prepolymer.
.sup.2 Tensile strength was determined according to ASTM D638.

TABLE B

Example.sup.5	%.sup.1 Wood Pulp	%.sup.1 Prepolymer	Addition Technique	Addition.sup.4	Sheet Appearance.sup.3 Stiffness	Homogeneity	Cushioning	Tensile Strength.sup.2 (psi)
19	64	36	A	C	1	4	3	346

CDD12547

20	64	36	B	C	3	1	2	217
21	64	36	A	D	4	3	1	34
22	71	29	A	C	2	2	4	345
23	59	41	B	C	1	1	5	548

A Pulp and prepolymer dispersions prepared separately and then mixed.
B Prepolymer dispersed directly into pulp slurry.
C Latex (GRS 2000) alum added to pulp slurry.
D Latex (GRS 2000) alum added to the combined pulp prepolymer slurry.
.sup.1 The percentages for wood pulp and prepolymer are based on the combined weight of these materials.
.sup.2 Tensile strength was determined according to ASTM D638.
.sup.3 Values for stiffness, homogeneity and cushioning were assigned based on manual inspection starting with a rating of 1 for the highest degree of stiffness, homogeneity or cushioning.
.sup.4 About 7.5 weight % of latex solids was employed in each run based on the combined weight of pulp, prepolymer and latex.
.sup.5 All Examples used Prepolymer 2.

TABLE C

Example.sup.4	%.sup.1 Wood Pulp Fibers	%.sup.1 Polyester	%.sup.1 Prepolymer	Relative Total Charge	Williams Freeness	Prepolymer Type	Sheet Appearance.sup.3 Stiff- ness.	Homo- geneity	Cushioning	Tensile.sup.2 Strength (psi)
20	64	0	36	1	8	2	2	2	4	217
23	59	0	41	0.87	8	2	1	1	5	548
24.sup.6	51	13	36	1	8	2	3	4	2	177
25	38	26	36	0.5	7	2	4	5	3	184
26	43	29	29	0.45	7	2	--	--	--	--.sup.5
27	38	26	36	0.5	5	2	5	3	1	140
28	38	26	36	0.5	5	1	--	--	--	--.sup.5

.sup.1 The % is based on the combined weight of pulp, polyester fibers an prepolymer employed.
.sup.2 Tensile strength was determined according to ASTM D638.
.sup.3 Values for stiffness, homogeneity and cushioning were assigned based on manual inspection starting with a rating of 1 for the highest degree of stiffness, homogeneity or cushioning.
.sup.4 Examples 20 and 23 are repeated from the preceding table.
.sup.5 As illustrated by Examples 26 and 28 it may be necessary to adjust the fiber mix employed to include less polyester fibers if a coherent

CDD12548

sheet is to be obtained.
.sup.6 In Examples 24-28 the prepolymer is dispersed directly into a dispersion of the fibers.

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CDD12549

United States Patent *3,971,785*
Messina , et al. **July 27, 1976**

Process for the manufacture of flowed-in aerosol can gaskets

Abstract

Process of lining aerosol can valve mounting cups with a gasketing composition comprising a carbon dioxide blocked polyamine dispersed in a liquid polyurethane prepolymer consisting of a free isocyanate group-containing reaction product of a polyisocyanate compound with a polyhydroxy material. The lined cups are heated for a few minutes to gel the gasket and full cure subsequently takes place without further intervention by means of ambient atmospheric moisture. The process is rapid, economical in equipment and produces gaskets which permit a significant extension of swaging specifications.

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Assignee: **W. R. Grace & Co.** (Cambridge, MA)
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Primary Examiner: Hoag; Willard E.
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CDD12550

Parent Case Text

This is a continuation of application Ser. No. 302,005 filed Oct. 30, 1972 and now abandoned.

Claims

What is claimed is:

1. A method for lining an aerosol can mounting cup with a sealing gasket consisting of:

a. depositing in the annular channel of the mounting cup a layer of a composition comprising (1) a liquid prepolymer of a free isocyanate groups-containing reaction product of a polyisocyanate with a polyhydroxy compound and (2) a finely divided carbon dioxide blocked polyamine;

b. heating the cup and said composition deposited therein to a temperature sufficient to cause decomposition of said polyamine with time, but said heating being for a time sufficient to gel said composition only and insufficient to cause substantial decomposition of said polyamine; and

c. then allowing said composition to cure further at ambient temperature in an atmosphere containing moisture.

2. The method of claim 1 wherein said heating temperature is under 200.degree.F and said heating time is about 2 minutes.

3. The method of claim 1 wherein the polyhydroxy compound is a mixture of at least one diol and one triol, said triol constituting at least 30% of the mixture by weight.

4. The method of claim 1 wherein the polyamine is a triamine and the polyisocyanate is aromatic or alicyclic.

Description

THE PRIOR ART

Pressurized aerosol containers are widely used for packaging and dispensing an ever larger variety of materials. In this type of application, the product to be dispensed is confined under pressure by means of a volatile propellant and is discharged in a controlled manner through a valve-actuated orifice. A typical aerosol unit comprises a hollow cylindrical container closed at one end and provided with an opening at its opposite end for receiving a dispensing valve assembly. A metal fitment or mounting cup serves as a closure for the container and also as a support for the valve assembly which is tightly fitted within an aperture centrally located in the cup.

The cup is swaged into the 1-inch standard opening of the aerosol can to produce a container that can safely withstand the internal pressure of the finished package and yet allows the convenient dispensing of the contents when the valve is actuated. An elastomeric sealing material, formed into a gasket by high

CDD12551

speed deposition into the annular channel of the mounting cup, compensates for the failure of the metal cup and can to mate perfectly at their juncture. The imperfect metal to metal juncture is the normal result of tolerances, in parts and in swaging process, which must be accepted in the production of an economically feasible aerosol package. Both the manufacturer of cup, valve and can and the aerosol packager who fills and swages the cup into the can must operate within certain allowable tolerances in order that a functional package be produced. In the swaging operation, the parameters of interest are known as crimping dimensions and specified as crimp depth and crimp diameter.

It has been found that the use of a polyurethane composition containing a polyamine carbamate, as the material for the sealing gaskets, has extended the allowable limits of the crimping dimensions beyond those permissible with conventional aerosol mounting cup systems such as the polychloroprene compositions described in U.S. Pat. No. 3,389,113.

The use of polyurethane gaskets per se in aerosol cans was first claimed by Siebel in British patent specification No. 1,203,384 in Oct. 1970. However, the practical problems associated with the high speed placement of gaskets into very large numbers of aerosol mounting cups have effectively kept this type of material from the industrial scene. Part of the reason for this lies in the alternative of using an active curing agent such as a polyamine, or omitting the curing agent and allowing the gasketing material to cure by means of ambient moisture. In the first instance, the inconvenience of a two-package system effectively discourages the cup manufacturer, while in the second instance relatively long cure times of 60 hours or more are needed, causing the accumulation of very large numbers of cups "in process" and thus increasing the requirements for equipment as well as the delay of quality control procedures which must be carried out on the gelled gaskets.

Furthermore, while carbon dioxide-blocked polyamines (carbamates) have been used as curing agents for polyurethane prepolymers to permit the formulation of stable one-package compositions that can be heat activated as desired, the potential advantages of such systems in aerosol mounting cup flowed-in gasket applications have remained largely unexplored. This state of affairs is perhaps due in part to the preponderant selection of diamine carbamates for curing linear polyurethanes destined to the production of filaments, and also in part to the undesirable release of carbon dioxide on heating. In any event, applicants have now discovered unexpected advantages, such as the extension of swaging tolerances already mentioned, in the use of certain polyurethane compositions for aerosol gasketing. These advantages, as well as others, will be fully described in the following disclosure.

SUMMARY OF THE INVENTION

According to the present invention, it has now become both possible and desirable to line aerosol can mounting cups with exceptional gaskets by a process which involves (1) the high speed placement into the annular channel of the cups of a stable one-package composition comprising a free-isocyanate group-containing reaction product of a polyhydroxy material with a polyisocyanate and a finely divided carbamate which is a carbon dioxide-blocked polyamine, (2) the heating of the flowed-in composition for a few minutes at the decomposition temperature of the carbamate to cause the gelling of the gasket material, (3) the subsequent curing of the gelled gasket material by ambient moisture during shipment to the aerosol packager, and (4) the swaging of the lined cups to the body of aerosol cans after the latter have been filled with the product to be dispensed.

The carbamate gelled, ambient moisture curing polyurethane aerosol cup gasketing system of the invention provides for, as shall be demonstrated, a substantial widening of allowable tolerances of crimping dimensions beyond those currently permitted in such an assembly, and a means of rapidly bringing a liquid prepolymer resin gasketing compound to a gelled and partially cured state sufficient so that the production quality of resulting gasket-cup assemblies can be observed within 5 minutes of the

CDD12552

compound placement.

DESCRIPTION OF THE DRAWINGS

The present invention will be more clearly understood on reference to the accompanying drawing and the discussion relating thereto:

FIG. 1 is a side elevational view of a typical aerosol container provided with a mounting cup and valve unit.

FIG. 2 is an axial sectional view of the aerosol mounting cup of FIG. 1 carrying a gasket perpared from compositions of the present invention.

FIG. 3 is a fragmentary axial sectional view of the upper portion of the aerosol container of FIG. 1 showing the gasketed mounting cup of FIG. 2 crimped in position over the mouth of the container.

Referring to FIG. 1, a typical aerosol container is illustrated which comprises a cylindrical body portion 10 fitted with a domed top portion 12 and a bottom closure 11. The container is provided with a metering valve generally designated at 13 which is actuated by button 15. The actuator button is carried on a hollow valve stem 14 and provided with an orifice 16 through which the container contents are discharged when valve 13 is opened. Communicating with valve 13 is a dip tube 17 of sufficient length to allow the contents to be discharged from the container. The valve unit, which may be any of the various types known to the art, is supported by a mounting cup, generally designated at 18, which is adapted to receive the valve stem 14. The mounting cup also serves as a closure for the container and carries the sealing gasket in the annular channel 22 which is applied over the opening in the domed top portion 12 of the container.

An axial sectional view of mounting cup 18 is shown in FIG. 2 in inverted position relative to its placement in the assembled container. The cup comprises a circular panel 19 having an integral skirt 20 depending from its periphery. The free edge of skirt 20 outwardly flanged at 21 to form an annular gasket-receiving channel 22. The inner portion of panel 19 is countersunk to form a tubular recess, generally designated at 23, which has a dependent circular wall 24 integrally joined with an apertured horizontal wall 25. When the cup is placed in sealing position, the tubular recess 23 acts as a pedestal for the valve unit and the valve stem is admitted into the container through apertured wall 25. The gasket 26 is disposed predominantly in the annular channel 22 of the cup.

FIG. 3 shows the gasketed mounting cup of FIG. 2 crimped in position over the mouth of an aerosol container. As illustrated in FIG. 3, the open end of domed portion 12 of the container is provided with an outwardly curled peripheral bead 27 which defines the container mouth. The annular channel 22 of the mounting cup embraces the bead 27 of the container so that the gasket 26 carried by channel 22 is positioned on bead 27. The lower portion of the skirt 20 is flared outwardly against the wall of domed portion 12 adjacent to the bead 27. The gasket forms a seal between the skirt and the wall adjacent to the container mouth. The crimping dimensions as measured from swaged seam 28 are identified on the drawing as the crimp depth and the crimp diameter.

DETAILED DESCRIPTION OF THE INVENTION

The compositions that are used in the process of this invention consist essentially of a low molecular weight polyurethane prepolymer into which there is dispersed a finely divided polyamine carbamate. Fillers, solvent, antioxidants, pigments and other additives for elastomers, which are free from active hydrogen, may be incorporated for the conventional effects. The usable prepolymers are low molecular

weight reaction products of polyisocyanates, preferably aromatic or alicyclic, with polyfunctional organic compounds containing active hydrogen, preferably polyhydroxy compounds. If desired, the isocyanate groups of the prepolymer themselves may be blocked, for instance with nonylphenol, to be freed later by heat, for reaction with the polyamine and moisture. The best results have been obtained with mixtures of triols and diols in which triol compounds constitute at least 30% of the total polyhydroxy compound mix weight.

The carbamates employed with the prepolymers are, as already mentioned, the reaction products of polyamines and carbon dioxide under anhydrous conditions. The compounds so prepared are generally stable solid materials which may be pulverized for dispersion into the polyurethane prepolymer or dispersed in an organic non-aqueous inert solvent prior to admixture with said prepolymer. The preferred particle size of the carbamate for mechanical stability of the prepolymer mix and the uniformity of the cured polyurethane mass is such that the powder should pass through a 200 mesh or finer U.S. Bureau of Standards screen. Typical examples of usable carbamates are provided in U.S. Pat. Nos. 3,029,227 and 3,344,175.

In the process of the invention, the annular channel of aerosol mounting cups is lined with the prepolymer-carbamate composition by means of appropriate high speed gasket lining machinery. This operation may proceed at rates of 150 or more cups per minute per lining station. After lining, the cups are routed through an oven in which the gasketing material is subjected to a sufficiently high temperature, e.g. 175.degree.F, to decompose the carbamate into its component polyamine and carbon dioxide. In a matter of minutes, usually 5 or less, the polyamine reacts with the prepolymer and gels it. Surprisingly, the carbon dioxide released does not adversely affect the relatively thick channel-confined aerosol gasket to an undesirable degree. The lined cups can be examined at that point for gasket defects and those acceptable are immediately packed for shipment to the aerosol packager. Complete cure of the gaskets subsequently takes place, without further intervention, through reaction of the polymer with ambient moisture during a period of 3 to 5 days.

The temperature at which the gasketing mixture will gel depends to a certain extent upon the nature of the polyhydroxy compound mix as well as on the decomposition point of the carbamate. Thus, although a temperature within the range of 150.degree. to 300.degree.F or higher can be used, gelling can generally be effected in about 2 minutes at temperatures under 200.degree.F.

One of the principal advantages of this method of lining cups over conventional methods lies in the early possibility of examining the cups for satisfactory lining. With a conventional aerosol gasketing system such as one based on polychloroprene for instance, a 5 to 6 hour curing cycle is required involving various stages of drying and curing in a convection type drying and curing oven. Thus, in order to produce gasketed mounting cups at high rates, the drying and curing process must be of exceptionally large capacity and, furthermore, the final production results cannot be fulled observed until tens of thousands of units or more have become involved. In such circumstances defects in composition or mechanical performance may be quite costly. With this in mind, it can readily be understood that the ability to evaluate the quality of the final product after only five minutes is a great improvement over the 5 or 6 hours processing delay normally experienced.

The process of the invention can be further advantageously characterized by a great reduction, if not complete elimination, of the quantity of solvents and other volatile products usually associated with gasketing compositions. A conventional polychloroprene composition, for instance, can contain up to 60% by weight of high boiling aromatic solvent, not to mention various additives such as plasticizers, curing agents and the like which either must be removed during the drying or are partly entrained or decomposed to noxious substances during the extended drying and curing process.

CDD12554

Subject to the preferences already expressed in terms of prepolymers, i.e. partial reaction products of cyclic diisocyanates with mixtures of diols and triols, such as polyalkylene glycols and polyhydroxy polyethers, there may be used other polyisocyanates and polyhydroxy compounds to achieve useful, if not optimum properties in the gaskets.

Among the polyisocyanates that may be employed in this manner are: the various unsubstituted phenylene diisocyanates, as well as those having one or more substituents such as methyl and other lower alkyl groups having up to about 4 carbon atoms, halogen atoms, nitro groups, alkoxy and aryloxy groups; various substituted and unsubstituted biphenylene diisocyanates; substituted and unsubstituted diphenyl diisocyanates such as the diphenylmethanes-, the diphenylisopropylidenes- and the diphenylsulfone diisocyanates; the naphthalene diisocyanates; alkylene diisocyanates containing up to about ten alkylene carbon atoms; cycloalkyl diisocyanates containing one or more cycloalkane rings such as 1,3-cyclopentene- and 4,4' -dicyclohexylmethane diisocyanate; and other diisocyanates such as 1-ethyleneisocyanato-4-phenyl-isocyanate. Examples of tri- and tetra- isocyanates that may be used include the benzene and toluene triisocyanates, 2-methyl-2-(4-isocyanatophenyl)-trimethylene diisocyanate, tetrakis-(4-isocyanatophenyl)methane and bis-(4-methyl-2,5-isocyanatophenyl) methane. Polymeric materials such as polymethylene polyphenylisocyanate may also be employed.

Suitable compounds that will react with the above isocyanates to yield the necessary prepolymers include polyols such as ethylene glycol, glycerol, pentaerythrytol, sorbitol, triethanolamine, as well as polymeric compounds such as polyglycols, polyhydroxy polyesters, polyhydroxy polyesteramides and polyhydroxy polyether oils.

Typical polyglycols include polyalkylene glycols, such as polyethylene glycol, polypropylene glycol, and polybutylene glycol.

Representative polyesters are reaction products of dihydric alcohols, such as ethylene glycol, diethylene glycol, tetraethylene glycol, 1,3-propylene glycol, dipropylene glycol, or higher polyhydric alcohols such as glycerol, trimethylol propane, pentaerythritol, mannitol, or mixtures of two or more of the alcohols with a polycarboxylic acid or anhydride such as succinic, adipic, glutaric, maloric, sebacic, azelaic, phthalic, terephthalic, isophthalic, trimellitic and pyromellitic acids and their anhydrides. Mixtures of the acids and anhydrides can be employed.

Illustrative polyhydroxy polyesteramides are the reaction products of a polyhydric alcohol with a dicarboxylic acid, examples of both of which have been mentioned above, and as necessary, diamines or amino-alcohols such as ethylene diamine, hexamethylene diamine, phenylene diamine, benzidine and monoethanolamine.

Examples of polyhydroxy polyethers include linear hydroxyl-containing polymers and copolymers of cyclic ethers such as ethylene oxide, epichlorohydrin, 1,2-propylene oxide, oxacyclobutane, and tetrahydrofuran, or branched polyethers obtained from the condensation of the aforementioned ethers with branched polyhydroxy compounds such as glycerol, 1,1-trimethylolpropane, pentaerythritol, sorbitol and sucrose. Mixtures of linear and branched polyethers or mixtures of polyesters and polyethers can also be employed.

Other polyhydroxy materials, for example, esters of hydroxycarboxylic acids, such as castor oil and glyceryl monoricinoleate, can also be used.

The solid polyurethane polyurea which results from the curing of the sealing compositions of interest may be crosslinked to any degree desired, depending on the number of functional groups present and the ratio of amino groups to isocyanate groups.

CDD12555

Satisfactory crosslinking of the polymers used in this invention is generally achieved with a carbamate to terminal insocyanate group chemical equivalent ratio of, for instance 0.5:1. These proportions may also vary more broadly depending on the particular nature of the components used and the degree of crosslinking required by the application intended for resulting polymer. Thus, ratios of 0.2:1 to 1.3:1 have been sucessfully employed with various formulations.

The compositions of the invention will generally contain a solvent to facilitate handling of the prepolymer mix by gasket-laying machinery. Usable solvents are organic liquids that do not possess any active hydrogen to react with the isocyanate groups of the polymer and are capable of either evaporating under process conditions or acting as plasticizers when left in the gasket. Examples of suitable liquids for this purpose include: aromatic hydrocarbons, such as benzene, toluene and xylene; acetic esters, such as ethyl and butyl acetates; chlorinated aromatic and aliphatic solvents, such as monochlorobenzene and carbon tetrachloride; ethers, such as butyl ethyl ether, dioxane and hydrofuran; and ethylene glycol monomethyl ether acetate. Solvents having active hydrogen such as the lower alcohols, may be used to prepare the carbamate, but they must be removed from the dispersion before it is mixed with the prepolymer. Relatively small quantities of solvent are needed for the gasketing compositions used in the process of the invention due to the liquid nature of the prepolymer. Thus, less than 10% by weight is generally sufficient. As a result, the pollution problem created during the drying of conventionally lined mounting cups as well as the precautionary equipment required to solve that problem are either minimized or eliminated. The latter advantage is fully realized when the solvent or diluting liquid selected doubles as a plasticizers and thus need not be removed from the composition. Certain high boiling esters, such as dioctyl and diisodecyl phthalate and the like, serve well in this capacity.

As fillers, there may be used, for example, calcium carbonate, calcium silicate, aluminum silicate, silica, chrysolite asbestos, carbon black, titanium dioxide, fully calcined clays and talcum powder. The latter material is preferred.

The following examples are provided to further illustrate the invention. All parts and percentages therein are on a weight basis, unless otherwise specified.

EXAMPLE 1

A stable prepolymer-carbamate composition is prepared from the following ingredients:

Component	Parts by Weight
Poly(oxypropylene)glycol, mol. weight 2,000 (POPS)	5.8
Poly(oxypropylene)triol, mol. weight 4,000 (POPT)	35.4
Tolylene diisocyanate (TDI)	5.7
Talc	39.9
Diethylenetriamine carbamate (DETAC), 33% solids	5.7
Xylene	6.4
Silicone Oil	1.1
	100.0

CDD12556

The hydroxy compounds, POPG and POPT, and the talc are first mixed in a steam-jacketed glass lined reactor. The mix is heated to 100.degree.C and the reactor evacuated to remove water. After complete removal of the water, the batch is cooled to 50.degree.C and the xylene is charged and mixed. TDI is then introduced while the reactor is brought to 80.degree.C. The reaction is carried on at that temperature until the isocyanate content of the prepolymer mixture reaches 2.9%. The reaction product is then cooled to 30.degree.C and the DETAC dispersion in e.g. xylene, as well as the silicone oil, are mixed in to complete the batch.

EXAMPLE 2

The liquid compound prepared according to Example 1 is applied at the rate of about 300 mg solid basis per cup to aerosol valve mounting cups by conventional aerosol gasketing equipment. Production rate for this operation is about 200 cups per minute per application nozzle. After the liquid has been applied to the cups, the latter are transferred by automatic belt feed mechanism to a small capacity oven for the gelling cycle. A "baby" size or "half" size Hurricane oven suffices for this operation. The gelling cycle on the moving belt through the oven lasts two minutes at 160.degree.F for the compound of Example 1. The cups are immediately packaged in shipping boxes. Full cure then takes place through ambient atmospheric moisture within 5 days.

EXAMPLE 3

To measure the effectiveness of sealing and swaging of the aerosol mounting cups on aerosol cans, tests were carried out on a commercial aerosol filling line with a number of different aerosol cup sealing gaskets. The history of loss of volatile contents of the test cans was recorded and the number of cans which failed to seal was noted.

The test was made at various crimping and swaging conditions, i.e. by varying the crimp diameter and the crimp depth (see FIG. 3 of the drawing). In the following table, the results of a test of cups made with the composition of Example 1 are compared to those of cups made with a polychloroprene compound such as that of Example 3 of U.S. Pat. No. 3,389,113 cured in the conventional manner.

Crimping Condition	Gasket Compound	
	Polychloroprene	Carbamate Gelled/Ambient Cure Polyurethane
I. Crimp Depth -- 0.160 inches Crimp Diameter 1.054 inches	0%	0%
II. Crimp Depth -- 0.205 inches Crimp Diameter -- 1.068 inches	14%	2%

CDD12557

Crimping condition I represents the optimum target conditions presently required to yield 100 percent satisfactory sealing. In this instance, both gaskets performed well. However, maintaining these optimum crimping conditions during high speed filling and sealing of aerosol cans is not always practical and thus some deviation always occurs yielding some cans which are not as tightly sealed as in condition I. These cans belong to crimping condition II. At this condition, the conventional gasket fails to seal more frequently than the carbamate gelled/ambient cure polyurethane aerosol cup gasket. This reduction in failing cans from 14% to 2% represents a significant improvement in sealing effectiveness and reduces the present rate for discarded and scrapped aerosol cans which leak through the crimped seam between the valve mounting cup and can.

EXAMPLES 4 TO 7

Other prepolymer-carbamate compositions were prepared for testing as in Example 3. These compositions generally comprised: about 40% of polyhydroxy compounds in various diol to polyol mix ratios; about 6 to 8% polyisocyanate, in these instances--dicyclohexylmethane diisocyanate; about 38% talc; about 5.5 to 6.0% carbamate (DETAC); about 4.5% xylene; and about 1.2% silicone oil. Some of the polyhydroxy compound mixes selected were as follows:

Polyhydroxy Compound Mixtures

Polyhydroxy Compound	Example 4	5	6	7
Poly(oxypropylene)glycol, 2000*	3.59	3.76	22.85	5.26
Poly(oxypropylene)glycol terminated with ethylene oxide, 4000		15.63		21.87
Poly(oxytetramethylene)glycol, 3000	1.76			
Poly(oxypropylene)triol, 3000	9.57	24.53		
Poly(oxypropylene)triol, 4000			4.94	16.20
Poly(oxypropylene)triol terminated with ethylene oxide, 6000	29.06		14.99	
Total Weight Percent	43.98	43.92	42.78	43.33

*molecular weight

After application to mounting cups and curing, the cups were swaged onto filled aerosol cans under the two crimping conditions of Example 3. Leakage tests again showed a significant improvement in sealing as compared to the conventional polychloroprene system.

In summary, the present invention relates to an aerosol gasketing system which not only benefits from the processing ease attending stable one-package fast-curing polyurethanes, but also performs in a

CDD12558

superior manner under the type of conditions generally availing in that field of packaging. Although a limited number of examples have been provided here to illustrate various operational features of the invention, it is apparent that the man skilled in the art can devise several other embodiments which will be substantially within the scope of the invention as described in the appended claims.

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